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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a battery having superior charge and discharge cycle characteristic such as high capacity, high energy and small irreversible capacity, even at quick charging and discharging by adding a calcium compound inside of a battery.

SOLUTION: As a main structural material of the negative electrode active material, carbon grains adhered with calcium compound is used. As a calcium compound to be adhered to the carbon grains, anhydride such as a halide and oxide is preferable, and a halide is more preferable. Most preferably is fluoride among halides, and CaF2 and CaF3 are used. As a carbon grain adhered with calcium compound for holding, any carbon grain as long as it is capable of storing and releasing lithium may be used, a carbon grain having a surface spacing (d002) especially by X-ray diffraction of 3.354-3.369 Å and crystal size in C-axial direction(Lc) of 200 Å preferable is preferable, since high capacity can be obtained.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the negative electrode for lithium secondary batteries which was applied to the lithium secondary battery, especially discharge capacity and whose power density are size and was excellent in the cycle property.
[0002]
[Description of the Prior Art] As a negative electrode of a lithium secondary battery, although the lithium metal and the lithium alloy had been used conventionally, that the short circuit and cycle life of positive/negative two poles by deposit (dendrite) of a resin-like lithium are short, and the degraded minute should be compensated for the reason, the lithium of the 3 time equivalent of cell capacity is required for these cells, and they had the defect that energy density was low. In order to solve these troubles recently, the research which uses a carbon particle for a negative electrode is active. When using this kind of negative electrode, especially the graphite to which graphitization progressed (for example, if a cobalt acid lithium is used for a positive electrode, when cell voltage will become a flat and it will use for the pocket device of cell use), it is predominant in respect of capacity. However, if high rate charge is performed using this graphite, the dope voltage at the time of charge will become the 0V neighborhood, and will become competitive reaction with a deposit of a lithium. therefore -- for example, the configuration in JP,5-299073,A is using as the electrode material the carbon complex which consists of covering with the film containing a VIII group's metallic element the surface of the high crystal carbon particle which forms the heart, and carbon covering a it top further, and since the surface area of an electrode is large, it supposes that charge-and-discharge capacity and charge-and-discharge speed improved remarkably, at the same time the carbon particle which has surface random layer structure by this helps the intercalation of a lithium. However, the irreversible capacity of the carbon of a negative-electrode carbon particle increased, and, as a result, energy density was not able to say that it was still enough.
[0003]
[Problem(s) to be Solved by the Invention] As mentioned above, when a carbon particle and composite are used as a negative electrode, there is a problem of the increment in a carbonaceous irreversible capacity or the difficulty of electrode manufacture. This invention aims at offering the lithium secondary battery which are high capacity and high energy density and excelled [constituent / in a negative-electrode active material / main] in the charge-and-discharge cycle property with little irreversible capacity at the time of rapid charge and discharge by using the carbon particle which carried out adhesion maintenance of the lime compound in order to solve this trouble.
[0004]
[Means for Solving the Problem] Although it was the reaction to which occlusion of a lithium to a carbon particle and emission (an intercalation, day intercalation) mainly take place when carbon was considered as a negative-electrode active material, it turned out that a coat condition produced between the electrolytic solution and the carbon surface is involving as one of the factors which govern the reaction. For example, it is precise, a high coat of ion conductivity is excellent also in the cell property, and it is known that an ion conductivity conversely thick low coat has bad rate property and cycle property so that it may be represented with a case where a lithium metal is used as a negative-electrode active material. In that case, the former is coats, such as a lithium carbonate and lithium oxide, and it is reported that the latters are coats, such as lithium fluoride. A coat which the same thing as this produces on the carbon surface is also considered. That is, formation of a low coat of ionic conductivity, such as lithium fluoride, is raised on the surface of a carbon particle as one of the factors which check the rate property of a carbon particle. this invention persons found out controlling that a fluorine anion which exists in the electrolytic solution by carrying out adhesion maintenance of the lime compound comes to the negative-electrode surface to an interface of the electrolytic solution and a carbon particle, as a result of examining many things, in order to solve a trouble about this coat.
[0005] Although it will not matter anything, for example, a halogenide, an oxide, a sulfate, a nitrate, etc. will be raised if it combines with calcium in a carbon particle as a lime compound which carries out adhesion maintenance, it is not limited to these. Preferably, it is anhydrides, such as a halogenide and an oxide, and is a halogenide still more preferably. It is a fluoride most preferably also in a halogenide and is CaF2. CaF3 It is raised. Although a method of processing chemically and electrochemically, carrying out adhesion maintenance of the lime compound itself by a mechano fusion etc., etc. are mentioned as the adhesion maintenance method of a lime compound after making the surface carry out adhesion maintenance of the lime compound by vacuum deposition, the sputtering method, wet reduction method, electrochemical reduction method, gaseous-phase reducing gas approach, laser ablation, etc., it is not limited to these.
[0006] an amount of a lime compound which carries out adhesion maintenance -- less than [30wt%] -- it is less than [10wt%] preferably. Furthermore, particle size of a lime compound by which adhesion maintenance was carried out has desirable 1 micrometer or less.
[0007] A spacing (d002) especially by X-ray diffraction method is 3.354 to 3.369 A, and since high capacity is obtained, a carbon particle whose magnitude (Lc) of a crystal of C shaft orientations is 200A or more is [that a carbon particle which carries out adhesion maintenance of the lime compound should just be a carbon particle which emits / occlusion and / a lithium] desirable.
[0008] As for a carbon particle used for this invention, it is desirable that it is the average grain size of 100 micrometers or less. When acquiring a predetermined configuration, a grinder and a classifier are used in order to obtain fine particles. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, counter JIETOMIRU, a revolution air-current mold jet mill, a screen,

etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification method, there is especially no limitation and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.

[0009] As a negative-electrode material which can be combined and can be used for this invention, an organic compound containing lithiums, such as a lithium metal, a lithium alloy, etc. and a chalcogen compound, methyl lithium, etc. is mentioned. Moreover, it is also possible by using together an organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in a carbon particle used for this invention beforehand.

[0010] a case where a carbon particle which carried out adhesion maintenance of the lime compound of this invention is used -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture. If it is the electronic conduction nature material which does not have a bad influence on cell engine performance as an electric conduction agent, it is good anything. Usually, conductive materials, such as natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and a conductive ceramic material, can be included as one sort or those mixture. In these, concomitant use of acetylene black and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0011] When using a carbon particle which carried out adhesion maintenance of the lime compound of this invention, a thing of the fine particles for which a surface layer portion is embellished with objects other than a lime compound at least is also possible. For example, applying technology, such as plating, sintering, a mechano fusion, and vacuum evaporationo, and carrying out the coat of the ion conductivity good material, such as good material of electronic conduction nature, such as gold, silver, carbon, nickel, and copper, and a lithium carbonate, boron glass, a solid electrolyte, is mentioned.

[0012] As a binder, polymer, polysaccharide, etc. which have thermoplastic trees, such as tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a carboxymethyl cellulose, and rubber elasticity can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and a binder which has an organic-functions machine which reacts, it is desirable like polysaccharide to methylate, for example and to carry out deactivation of the functional group. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[0013] If it is the material which does not have a bad influence on cell engine performance as a filler, it is good anything. Usually, olefin system polymer, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. An addition of a filler has 0 - 30 desirable % of the weight.

[0014] If it is the electronic conductor which does not do a bad influence in a constituted cell as a charge collector of an electrode active material, it is good anything. For example, as a charge collector for positive electrodes, besides aluminum, titanium, stainless steel, nickel, baking carbon, a conductive polymer, electrically conductive glass, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and an object which processed the surfaces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As a charge collector for negative electrodes, besides copper, stainless steel, nickel, aluminum, titanium, baking carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and an object which processed the surfaces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About these materials, it is also possible to oxidize the surface. About these configurations, the shape of the shape of the shape of others and a film and a sheet and a network, punch or an object by which expanded one was carried out, a lath object, a porosity object, a firing object, an organizer of a fiber group, etc. are used. [shape / of foil] Although especially limitation is thin, a 1-500-micrometer thing is used.

[0015] Thus, a negative electrode which used as the main constituent in a negative-electrode active material a carbon particle which carried out adhesion maintenance of the lime compound can be obtained. on the other hand -- as positive active material -- a metallic oxide of MnO2, MoO3, V2 O5, Lix CoO2, Lix NiO2, and Lix Mn2 O4 grade, and TiS2, MoS2 and NbSe3 etc. -- various kinds of material in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, and the poly aniline, and a conductive polymer, and an anion.

[0016] a viewpoint of [when using a carbon particle which carried out adhesion maintenance especially of the lime compound of this invention as a negative-electrode active material] high energy density to V2 O5, MnO2, Lix CoO2, Lix NiO2, and Lix Mn 2O4 etc. -- what has electrode potential of 3-4V is desirable. especially -- Lix CoO2, Lix NiO2, and Lix Mn 2O4 etc. -- a lithium content transition-metals oxide is desirable.

[0017] Moreover, it is desirable to be able to be as an electrolyte, for example with organic electrolysis liquid, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., and to use organic electrolysis liquid also in this. As an organic solvent of this organic electrolysis liquid, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Substitute tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, Dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO4, LiPF6, LiBF4, LiAsF6, LiCF3 SO3, and LiN (CF3 SO2)2 etc. -- it is mentioned. On the other hand, an object which melted the above supporting-electrolyte salts as a solid polymer electrolyte into polymer, such as polyethylene oxide, the bridge formation object and poly FOSUFAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li3 N and LiI, are also usable. That is, what is necessary is just nonaqueous electrolyte of lithium ion conductivity.

[0018] As a separator, transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. A sheet built from organic solvent-proof nature and hydrophobicity from polymer of olefin systems, such as polypropylene and polyethylene, a glass fiber, polyvinylidene fluoride, polytetrafluoroethylene, etc., a micropore film, and a nonwoven fabric are used. An aperture of a separator is a thing of a range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of a range generally used for a cell, for example, is 5-300 micrometers.

[0019] As a reason a charge-and-discharge property, especially whose rate property improve, although it is not necessarily clear, it is considered as follows. Generally, in the interior of a cell, various impurities which do not participate in charge and discharge of a cell are included in many cases. For example, LiPF6 When using for an electrolyte, the salt itself can carry in an impurity or it is possible to produce HF (fluoric acid) reacting with water of ultralow volume contained in the interior of a cell, or a solvent. Although an ion

conductivity high coat like a lithium carbonate is formed between the electrolytic solution and a carbon particle on the carbon particle surface in the case of lithium occlusion, if an acid like fluoric acid exists after the time of this coat formation, or formation, ion conductivity low lithium halide will be produced. Lithium halide produced in an interface of a carbon particle and the electrolytic solution bars occlusion emission of a lithium, and is considered to be one of the causes which, as a result, reduces the rate property of a negative electrode. Then, it tried thinking that this problem will be solvable and making a carbon particle carry out adhesion maintenance of the lime compound by not allowing fluoric acid to come near and making it an interface of a carbon particle and the electrolytic solution. Consequently, since improvement in a rate property of a negative electrode was checked when it expected that occlusion of a halogen anion, especially the fluorine anion will be carried out itself, or it would make [the calcium fluorine compound did not allow fluoric acid to come near, and] it a carbon particle and an electrolytic-solution interface according to the ion effect, it resulted in this invention.

[0020]

[Example] Hereafter, this invention is explained based on an example.

[0021] (Example 1) The artificial graphite (particle size of 6 micrometers) was dipped in the aqueous solution made to dissolve a calcium carbonate in a hydrofluoric acid, after condensing this, it dried at 110 degrees C, and the vacuum drying was carried out at 200 more degrees C for 16 hours. According to the chemical analysis, the amount of adhesion maintenance of the lime compound of the obtained powder A was 8.5% of the weight of the amount of adhesion maintenance to 10.0% of the weight of the charge presentation. Moreover, when fluorescence-X-rays diffraction investigated the lime compound's existence condition, the peak pattern of the calcium origin was detected. Next, when the distributed condition of a lime compound was observed by energy dispersion mold electron probe microanalysis (EPMA), the lime compound was distributed all over the artificial graphite, and was condensed a little in the end-face section of an artificial particle. When the magnitude of a lime compound particle was furthermore observed with the transmission electron microscope, several 100A particle was distributing to homogeneity mostly.

[0022] (Example 2) The coin mold nonaqueous electrolyte cell shown in drawing 1 as follows was made as an experiment, using the powder A obtained in the above-mentioned example 1 as a negative-electrode active material. A negative-electrode active material and polytetrafluoroethylene powder were mixed by the weight ratio 95:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.1mm in the shape of a sheet with the roller press. Next, this was dried at 200 degrees C under punching and reduced pressure in a circle with a diameter of 16mm for 15 hours, and the negative electrode 2 was obtained. The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached.

[0023] A positive electrode 1 is LiCoO2 as positive active material. Acetylene black and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. Next, this was dried at 200 degrees C under punching and reduced pressure in a circle with a diameter of 16mm for 15 hours, and the positive electrode 1 was obtained. The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. It is LiPF6 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porosity film made from polypropylene was used for the separator 3 using the electrolytic solution which carried out 1 mol/l dissolution. The coin mold lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. Let the cell using this powder A be a cell (A).

[0024] (Example of a comparison) Instead of Powder A, the cell was produced like the example 2 using powder B ** which is an artificial graphite (particle size of 6 micrometers) except it as a negative-electrode active material. Let the obtained cell be a comparison cell (B).

[0025] The charge and discharge test was performed using these cells (A) and (B). Charge-and-discharge speed set 100mA per 1g of carbon, 200mA, and bound potential of charge and discharge to 1.0V and 0.01V, respectively. The metal was shown for the result of the discharge capacity of obtained 5 cycle eye in a table 1.

[0026]

[A table 1]

電池	充放電速度(100mA/g)における放電容量(mAh/g)	充放電速度(200mA/g)における放電容量(mAh/g)
(A)	300	290
(B)	300	250

[0027] Although a difference will not be looked at by the discharge capacity when charge-and-discharge speed is 100mA per 1g of carbon if the cell (A) and comparison cell (B) using Powder A and Powder B are compared, when charge-and-discharge speed is 200mA per 1g of carbon, it turns out that the direction of this invention cell (A) using Powder A has a large discharge capacity compared with a comparison cell (B). Although the reason is not certain about these phenomena, when using for the main constituent in a negative-electrode active material the carbon particle which carried out adhesion maintenance of the lime compound, it is thought that the condition of the electrolytic solution and the interface which happens between the solute and material-list side especially is involving. That is, in the case of the powder B which is the carbon particle which has not carried out adhesion maintenance of the lime compound used conventionally, the coat on the surface of carbon produced in occlusion emission of a lithium etc. produces lithium halide at reacting to the interior of a cell with the hydrogen halide which exists in a minute amount, and is considered that the rapid charge-and-discharge property fell by the fall of whenever [ionic conduction]. The hydrogen halide which exists in the main constituent in a negative-electrode active material inside a cell on the other hand at a minute amount in the case of the powder A which is the carbon particle which carried out adhesion maintenance of the lime compound can be caught before reaching the interface of a carbon particle and the electrolytic solution, or it is possible that there

is work which protects the coat of a carbon particle from hydrogen halide with the ion effect of a halogenide.
[0028] Furthermore, it is thought that only the fall of ionic conductivity was able to be controlled, without increasing the reaction which occurs by the interface of a carbon particle and the electrolytic solution, since a difference was hardly seen if the initial charge-and-discharge effectiveness of a cell (A) and a comparison cell (B) is compared. In the above-mentioned example, although mentioned to the main constituent in a negative-electrode active material about the carbon particle which carried out adhesion maintenance of the calcium fluoride, the same effect was checked about other lime compounds. Furthermore, the same effect was seen also when a lime compound was added inside a lithium secondary battery. In addition, this invention is not limited to the start raw material, the manufacture method, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.
[0029]
[Effect of the Invention] Since this invention is constituted like ****, there are few falls of the ionic conductivity in a negative-electrode active material interface, as a result, its rapid charge-and-discharge property improves, and its cycle property also improves. Moreover, since the processing is easy and cheap, it is the method of reforming which was excellent in the negative-electrode material, and the cells obtained as a result are high capacity and high energy density also in rapid charge and discharge, and show the outstanding charge-and-discharge cycle property with little irreversible capacity.

[Translation done.]